

# H<sub>2</sub>XP:OH<sub>2</sub> Complexes: Hydrogen *vs.* Pnicogen Bonds

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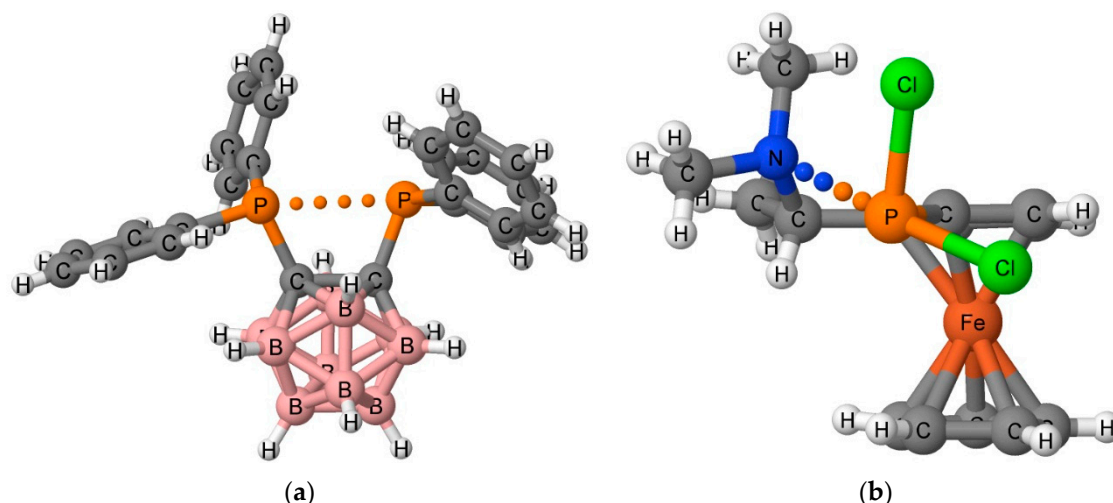
**Abstract:** A search of the Cambridge Structural Database (CSD) was carried out for phosphine-water and arsine-water complexes in which water is either the proton donor in hydrogen-bonded complexes, or the electron-pair donor in pnicogen-bonded complexes. The range of experimental P-O distances in the phosphine complexes is consistent with the results of *ab initio* MP2/aug'-cc-pVTZ calculations carried out on complexes H<sub>2</sub>XP:OH<sub>2</sub>, for X = NC, F, Cl, CN, OH, CCH, H, and CH<sub>3</sub>. Only hydrogen-bonded complexes are found on the H<sub>2</sub>(CH<sub>3</sub>)P:HOH and H<sub>3</sub>P:HOH potential surfaces, while only pnicogen-bonded complexes exist on H<sub>2</sub>(NC)P:OH<sub>2</sub>, H<sub>2</sub>FP:OH<sub>2</sub>, H<sub>2</sub>(CN)P:OH<sub>2</sub>, and H<sub>2</sub>(OH)P:OH<sub>2</sub> surfaces. Both hydrogen-bonded and pnicogen-bonded complexes are found on the H<sub>2</sub>CIP:OH<sub>2</sub> and H<sub>2</sub>(CCH)P:OH<sub>2</sub> surfaces, with the pnicogen-bonded complexes more stable than the corresponding hydrogen-bonded complexes. The more electronegative substituents prefer to form pnicogen-bonded complexes, while the more electropositive substituents form hydrogen-bonded complexes. The H<sub>2</sub>XP:OH<sub>2</sub> complexes are characterized in terms of their structures, binding energies, charge-transfer energies, and spin-spin coupling constants <sup>2h</sup>J(O-P), <sup>1h</sup>J(H-P), and <sup>1j</sup>J(O-H) across hydrogen bonds, and <sup>1p</sup>J(P-O) across pnicogen bonds.

**Keywords:** hydrogen bonds; pnicogen bonds; CSD; *ab initio* calculations; structures and binding energies; charge-transfer energies; EOM-CCSD spin-spin coupling constants

## 1. Introduction

Chloroform, dichloromethane, and water have been observed as solvent molecules in X-ray structures of crystals [1–6]. Such structures have long been used as a tool for identifying and confirming the presence of weak intermolecular interactions. The most prevalent intermolecular interaction in the Cambridge Structural Database (CSD) is the X-H...Y hydrogen bond, which has been at the forefront of intermolecular interactions since Pimentel's book "The Hydrogen Bond" [7]. The hydrogen bond is defined as an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation [8,9]. Of particular interest are the hydrogen bonds in the X-ray structures of organic hydrates. Hydrogen bonds involving water molecules interacting with different chemical groups have been identified and classified [3–6].

A relatively new intermolecular interaction, the pnicogen bond, was initially detected in the crystal structures of 1,2-dicarba-*closo*-dodecaboranes [10,11] and aminoalkyl-ferrocenylphosphanes [12]. The structures of two of these complexes are illustrated in Figure 1. A large number of intermolecular and intramolecular pnicogen interactions have also been observed in the solid phase [13–15]. Pnicogen bonds were first described theoretically for model complexes [16,17], and subsequent studies confirmed the stabilizing nature of pnicogen interactions [18–20]. The pnicogen bond is a Lewis acid-Lewis base interaction in which the Lewis acid is a group 15 element (N, P, As, or Sb) acting as an electron-pair acceptor.



**Figure 1.** X-ray structure of Cambridge Structural Database (CSD) Refcodes (a) XEBBEM01 and (b) QEZDOP. The pnictogen bond interaction is indicated with dots.

In the present article, we present the results of our search of the CSD for phosphine-water and arsine-water complexes in which water is either the proton donor in hydrogen-bonded complexes, or the electron-pair donor in pnictogen-bonded complexes. We also report the results of *ab initio* calculations on a series of complexes  $H_2XP:OH_2$ , for  $X = NC, F, Cl, CN, OH, CCH, H$ , and  $CH_3$ , stabilized by either hydrogen bonds or pnictogen bonds. We present and discuss the structures, binding energies, and charge-transfer energies of these complexes, as well as equation-of-motion coupled cluster singles and doubles (EOM-CCSD) spin–spin coupling constants across hydrogen bonds and pnictogen bonds.

## 2. Methods

### 2.1. Cambridge Structural Database Search

The Cambridge Structural Database [21] version 5.36 with updates from November 2014, February 2015, and May 2015 was searched for complexes that contain P(III) and As(III) with water molecules. Included structures have a distance of 2.0 to 4.0 Å between the pnictogen atom and the oxygen atom of water.

### 2.2. Ab Initio Calculations

The structures of the isolated monomers and the binary complexes  $H_2XP:OH_2$  were optimized at second-order Møller-Plesset perturbation theory (MP2) [22–25] with the aug'-cc-pVTZ basis set [26]. This basis set is derived from the Dunning aug-cc-pVTZ basis set [27,28] by removing diffuse functions from H atoms. Frequencies were computed to establish that the optimized structures correspond to equilibrium structures on their potential surfaces. Optimization and frequency calculations were performed using the Gaussian 09 program [29]. The binding energies ( $\Delta E$ ) of all complexes have been calculated as the total energy of the complex minus the sum of the total energies of the corresponding isolated monomers.

The electron densities of complexes have been analyzed using the Atoms in Molecules (AIM) methodology [30–33] employing the AIMAll [34] program. The topological analysis of the electron density produces the molecular graph of each complex. This graph identifies the location of electron density features of interest, including the electron density ( $\rho$ ) maxima associated with the various nuclei, and saddle points which correspond to bond critical points (BCPs). The zero gradient line which connects a BCP with two nuclei is the bond path.

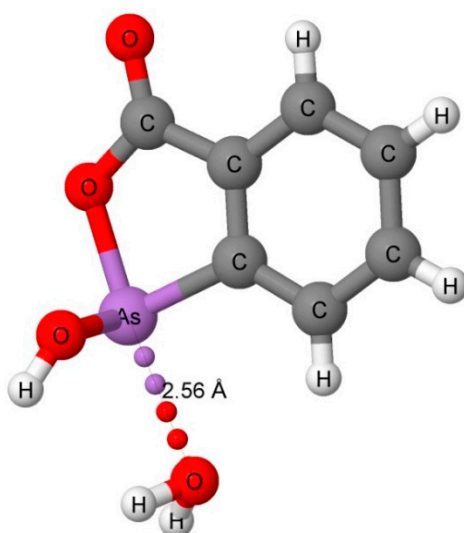
The Natural Bond Orbital (NBO) [35] method has been used to analyze the stabilizing charge-transfer interactions using the NBO6 program [36]. Since MP2 orbitals are nonexistent, the charge-transfer interactions have been computed using the B3LYP functional [37,38] with the aug'-cc-pVTZ basis set at the MP2/aug'-cc-pVTZ complex geometries, so that at least some electron correlation effects could be included.

Spin-spin coupling constants were evaluated using the EOM-CCSD method in the CI (configuration interaction)-like approximation [39,40], with all electrons correlated. For these calculations, the Ahlrichs [41] qzp basis set was placed on  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ , and  $^{19}\text{F}$ , and the qz2p basis set on  $^{31}\text{P}$ ,  $^{35}\text{Cl}$ , and hydrogen-bonded  $^1\text{H}$  atoms. The Dunning cc-pVDZ basis set was placed on all other  $^1\text{H}$  atoms. All terms, namely, the paramagnetic spin-orbit (PSO), diamagnetic spin orbit (DSO), Fermi contact (FC), and spin dipole (SD), have been evaluated. The EOM-CCSD calculations were performed using ACES II [42] on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

### 3. Results and Discussion

#### 3.1. CSD Search

The CSD search found only three water-phosphine complexes and seven water-arsine complexes that have a distance of 2.0 to 4.0 Å between the pnictogen atom and the oxygen atom of water. Two of the water-phosphine complexes are hydrogen bonded (CSD Refcodes: AGAHIB and BEZTOR) with  $\text{P} \cdots \text{H}$  distances of 2.48 and 2.72 Å, and  $\text{P} \cdots \text{O}$  distances of 3.315 and 3.465 Å, respectively. The third structure (NOPYEX) corresponds to a pnictogen-bonded complex between a triphenylphosphine derivative and water with a longer  $\text{P} \cdots \text{O}$  distance of 3.76 Å. Four of the water-arsine complexes (TELFAR, NOPYAT, FUTDUU, and IBAKIH) are pnictogen-bonded, and three (NIVWAQ, FUTDUU, and HAVKEW) are hydrogen-bonded. The pnictogen-bonded complex TELFAR which is illustrated in Figure 2 has a short As-O pnictogen bond distance of 2.56 Å. The O-As-O angle is  $171^\circ$ , which allows for the interaction of the O of water with the  $\sigma$ -hole of As. The short distance for this bond suggests that it has significant covalent character. The  $\text{As} \cdots \text{O}$  distances in the other pnictogen-bonded complexes range between 3.61 and 3.78 Å. The hydrogen-bonded complexes have  $\text{As} \cdots \text{H}$  distances between 2.81 and 3.22 Å, and  $\text{As} \cdots \text{O}$  distances between 3.70 and 3.96 Å.



**Figure 2.** The X-ray structure of CSD Refcode: TELFAR showing the  $\text{As} \cdots \text{O}$  pnictogen bond interaction.

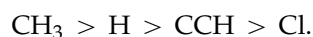
#### 3.2. Computational Results

We have attempted to optimize eight complexes  $\text{H}_2\text{XP}:\text{HOH}$  with  $\text{O}-\text{H} \cdots \text{P}$  hydrogen bonds, and eight complexes with  $\text{P} \cdots \text{O}$  pnictogen bonds, with  $\text{X} = \text{NC}$ ,  $\text{F}$ ,  $\text{Cl}$ ,  $\text{CN}$ ,  $\text{OH}$ ,  $\text{CCH}$ ,  $\text{H}$ , and  $\text{CH}_3$ .

However, only four hydrogen-bonded (HB) and six pnictogen-bonded (ZB) equilibrium complexes have been found on the potential surfaces. The structures, total energies, and molecular graphs of these complexes are reported in Table S1 of the Supporting Information, and their binding energies are given in Table 1. ZB complexes have binding energies which vary from  $-11.3$  to  $-21.1$   $\text{kJ}\cdot\text{mol}^{-1}$ , while HB complexes have binding energies between  $-9.4$  and  $-15.4$   $\text{kJ}\cdot\text{mol}^{-1}$ . The absolute values of the binding energies of the ZB complexes decrease in the order



while those of the HB complexes decrease in the reverse order



It is apparent from Table 1 that the more electronegative substituents prefer to form pnictogen-bonded complexes, while the more electropositive substituents form hydrogen-bonded complexes. This trend follows the general trend of the Molecular Electrostatic Potential (MEP) values around the phosphorous atom [43].  $\text{H}_2\text{ClP}$  and  $\text{H}(\text{CCH})\text{P}$  form both hydrogen-bonded and pnictogen-bonded complexes with  $\text{H}_2\text{O}$ , with the latter more stable by 7.9 and 0.5  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively.

**Table 1.** Binding energies of equilibrium pnictogen-bonded (ZB) and hydrogen-bonded (HB) complexes of  $\text{H}_2\text{XP}$  with  $\text{H}_2\text{O}$ .

$\text{H}_2\text{XP}$ , X =	Binding Energies ( $\Delta E$ , $\text{kJ}\cdot\text{mol}^{-1}$ )	
	ZB	HB
NC	-21.1	
F	-19.5	
Cl	-17.3	-9.4
CN	-16.9	
OH	-12.8	
CCH	-11.3	-10.8
H		-11.1
$\text{CH}_3$		-15.4

### 3.2.1. Hydrogen-Bonded Complexes

Only four equilibrium hydrogen-bonded complexes have been found on the  $\text{H}_2\text{XP}:\text{HOH}$  surfaces; namely,  $\text{H}_2\text{ClP}:\text{HOH}$ ,  $\text{H}_2(\text{CCH})\text{P}:\text{HOH}$ ,  $\text{H}_3\text{P}:\text{HOH}$ , and  $\text{H}_2(\text{CH}_3)\text{P}:\text{HOH}$ . The binding energies of these are given in Table 1, and selected structural parameters are reported in Table 2. The shortest intermolecular  $\text{O}\cdots\text{P}$  and  $\text{H}\cdots\text{P}$  distances are 3.360 and 2.536 Å, respectively, in  $\text{H}_2(\text{CH}_3)\text{P}:\text{HOH}$ . The remaining three complexes have  $\text{O}\cdots\text{P}$  distances between 3.55 and 3.59 Å, and  $\text{H}\cdots\text{P}$  distances between 2.62 and 2.66 Å. These distances are consistent with the experimental distances from the CSD. As evident from Table 2, the hydrogen bonds in  $\text{H}_2(\text{CCH})\text{P}:\text{HOH}$  and  $\text{H}_3\text{P}:\text{HOH}$  are close to linear, with  $\text{H}-\text{O}-\text{P}$  angles of  $7^\circ$ , while these bonds in  $\text{H}_2\text{ClP}:\text{HOH}$  and  $\text{H}_2(\text{CH}_3)\text{P}:\text{HOH}$  are nonlinear with values of  $19^\circ$  and  $27^\circ$ , respectively. Moreover, the  $\text{H}_2\text{O}$  molecule is positioned similarly in  $\text{H}_2\text{ClP}:\text{HOH}$  and  $\text{H}_2(\text{CCH})\text{P}:\text{HOH}$ , but has a different orientation in  $\text{H}_3\text{P}:\text{HOH}$  and  $\text{H}_2(\text{CH}_3)\text{P}:\text{HOH}$ , as illustrated in Figure 3. In these two complexes, but particularly  $\text{H}_2(\text{CH}_3)\text{P}:\text{HOH}$ , there appears to be an attractive interaction between the water oxygen and the hydrogens of the substituent. All of these differences lead to a lack of correlation between the binding energies of these complexes and the  $\text{O}\cdots\text{P}$  distances. However, the electrostatic minimum associated with the lone pair of the phosphorous atom [43] and the  $\text{H}\cdots\text{P}$  distances do correlate. Although not included in Tables 1 and 2 there is an equilibrium hydrogen-bonded complex formed between  $\text{H}_2(\text{OH})\text{P}$  and  $\text{H}_2\text{O}$  with a binding energy of  $-28.5$   $\text{kJ}\cdot\text{mol}^{-1}$ . However, it is stabilized by an  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond with the substituent  $\text{O}-\text{H}$  as the proton donor to  $\text{H}_2\text{O}$ .

**Table 2.** O...P, H...P, and O-H distances, and H-O-P angles for hydrogen-bonded complexes H<sub>2</sub>XP:HOH with C<sub>s</sub> symmetry.

H <sub>2</sub> XP, X =	Distance (R, Å)			Angles (<, °)
	R(O...P)	R(H...P)	R(O-H) <sup>a</sup>	<H-O-P
Cl	3.553	2.656	0.965	19
CCH	3.585	2.629	0.966	7
H	3.575	2.620	0.966	7
CH <sub>3</sub>	3.360	2.536	0.967	27

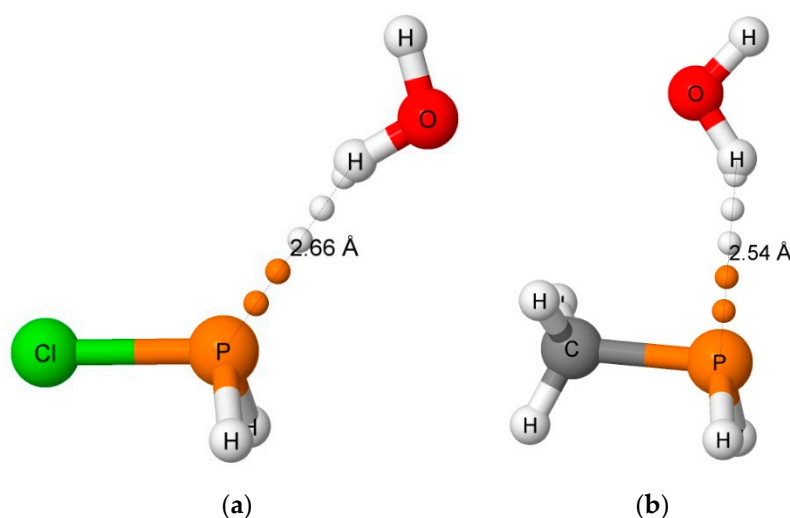
(a) The O-H distance in isolated H<sub>2</sub>O is 0.961 Å.**Figure 3.** The hydrogen-bonded complexes H<sub>2</sub>ClP:HOH (a) and H<sub>2</sub>(CH<sub>3</sub>)P:HOH (b). The orientation of the H<sub>2</sub>O molecule in H<sub>2</sub>(CCH)P:HOH is similar to that in H<sub>2</sub>ClP:HOH, while the orientation of H<sub>2</sub>O in H<sub>3</sub>P:HOH is similar to that in H<sub>2</sub>(CH<sub>3</sub>)P:HOH.

Table 3 presents the stabilizing NBO  $P_{lp} \rightarrow \sigma^*H-O$  charge-transfer energies for the four hydrogen-bonded complexes. These energies range from 9 kJ·mol<sup>−1</sup> for H<sub>2</sub>ClP:HOH to between 14 and 15 kJ·mol<sup>−1</sup> for the remaining complexes. The charge-transfer energies do not correlate with either the O...P or the H...P distances.

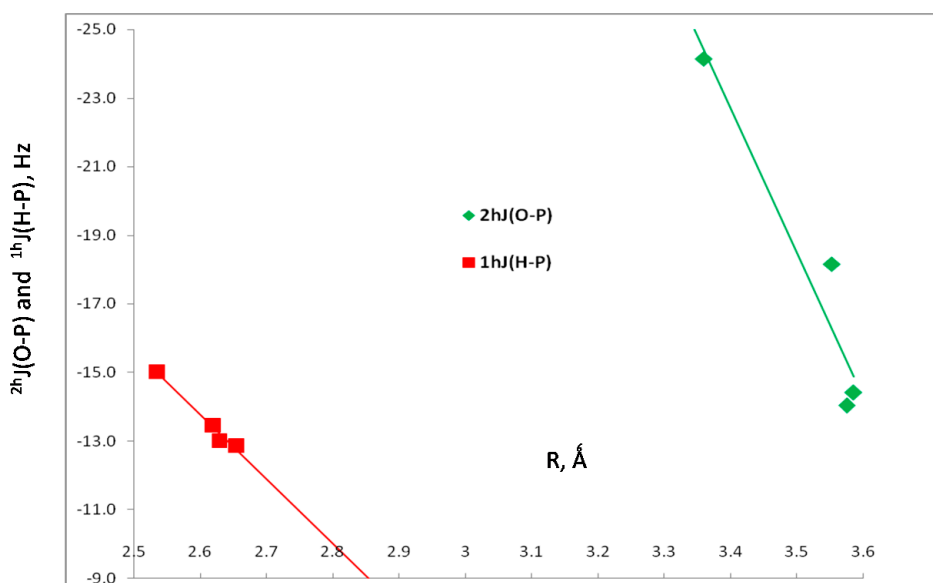
**Table 3.** Charge-transfer energies ( $P_{lp} \rightarrow \sigma^*H-O$ ) and coupling constants  $^2J(O-P)$ ,  $^1J(H-P)$ , and  $^1J(O-H)$  for hydrogen-bonded complexes H<sub>2</sub>XP:HOH.

H <sub>2</sub> XP, X =	Charge-Transfer Energies (kJ·mol <sup>−1</sup> )	Coupling Constants (Hz)		
	$P_{lp} \rightarrow \sigma^*H-O$ <sup>a</sup>	$^2J(O-P)$	$^1J(H-P)$	$^1J(O-H)$ <sup>b</sup>
Cl	9.0	−18.2	−12.9	−78.0
CCH	13.8	−14.4	−13.0	−77.9
H	14.0	−14.0	−13.5	−78.1
CH <sub>3</sub>	15.0	−24.1	−15.0	−78.4

<sup>a</sup> The  $O_{lp} \rightarrow \sigma^*H-O$  charge-transfer energy in the complex of H<sub>2</sub>(OH)P with H<sub>2</sub>O that has the substituent O-H as the proton donor is 41.0 kJ·mol<sup>−1</sup>; <sup>b</sup>  $^1J(O-H)$  in isolated H<sub>2</sub>O is −77.0 Hz.

The two-bond coupling constant  $^2J(O-P)$  and the one-bond coupling constant  $^1J(H-P)$  across the hydrogen bonds, and the one-bond coupling constant  $^1J(O-H)$  for the hydrogen-bonded O-H group are also reported in Table 3. The components of these coupling constants are reported in Table S2

of the Supporting Information. Values of  ${}^2\text{hJ}(\text{O-P})$  vary from  $-14$  to  $-24$  Hz, while values of  ${}^1\text{hJ}(\text{H-P})$  lie between  $-13$  and  $-15$  Hz. The dependence of these two coupling constants on the corresponding  $\text{O}\cdots\text{P}$  and  $\text{H}\cdots\text{P}$  distances is shown graphically in Figure 4. Since there are only 4 points in each set and at least two of them have similar values of the coupling constant and the corresponding distance, only linear trendlines were used to illustrate the distance dependence. The correlation coefficients of these trendlines are 0.915 for  ${}^2\text{hJ}(\text{O-P})$  and 0.973 for  ${}^1\text{hJ}(\text{H-P})$ . The third coupling constant,  ${}^1\text{J}(\text{O-H})$  has a value of  $-77.0$  Hz in the isolated  $\text{H}_2\text{O}$  molecule, and increases in absolute value only slightly upon complex formation to between  $-77.9$  and  $-78.4$  Hz. The O-H distance of  $0.961$  Å in the monomer also increases only slightly upon complexation, with values between  $0.965$  and  $0.967$  Å. The one-bond coupling constant  ${}^1\text{J}(\text{O-H})$  for the non-hydrogen-bonded O-H decreases to about  $-62$  Hz.



**Figure 4.**  ${}^2\text{hJ}(\text{O-P})$  versus the  $\text{O}\cdots\text{P}$  distance, and  ${}^1\text{hJ}(\text{H-P})$  versus the  $\text{H}\cdots\text{P}$  distance for HB complexes  $\text{H}_2\text{XP}:\text{HOH}$ .

### 3.2.2. Pnictogen-Bonded Complexes

Three of the six equilibrium pnictogen-bonded  $\text{H}_2\text{XP}:\text{OH}_2$  complexes have  $\text{C}_s$  symmetry with the  $\text{H}_2\text{O}$  molecule in the symmetry plane, and three have  $\text{C}_1$  symmetry. For reasons of computational efficiency, particularly for the coupling constant calculations, we have re-optimized the  $\text{C}_1$  structures under the constraint of  $\text{C}_s$  symmetry with an in-plane  $\text{H}_2\text{O}$  molecule. The binding energies of  $\text{C}_1$  and  $\text{C}_s$  structures are compared in Table 4. The  $\text{C}_s$  structures of  $\text{H}_2\text{FP}:\text{OH}_2$ ,  $\text{H}_2\text{ClP}:\text{OH}_2$ , and  $\text{H}_2(\text{OH})\text{P}:\text{OH}_2$  with  $\text{H}_2\text{O}$  in the  $\text{C}_s$  symmetry plane are only  $0.1$  to  $0.4$   $\text{kJ}\cdot\text{mol}^{-1}$  less stable than the  $\text{C}_1$  equilibrium structures. Moreover, the ordering of complexes according to decreasing binding energy is the same for the equilibrium structures and those with  $\text{C}_s$  symmetry, and the structures of  $\text{C}_1$  and corresponding  $\text{C}_s$  complexes are very similar. To ensure that there are no other pnictogen-bonded complexes with  $\text{P}\cdots\text{O}$  pnictogen bonds, we also optimized a set of these complexes with  $\text{C}_s$  symmetry in which the  $\text{H}_2\text{O}$  molecule does not lie in the symmetry plane. All of these complexes have one imaginary frequency, and smaller absolute values of the binding energies than the complexes with in-plane  $\text{H}_2\text{O}$  molecules, as evident from Table 4. The two types of  $\text{C}_s$  complexes are illustrated in Figure 5.

The structures, total energies, and molecular graphs of the three pnictogen-bonded ZB complexes  $\text{H}_2\text{XP}:\text{OH}_2$  with  $\text{C}_s$  symmetry, one imaginary frequency, and in-plane  $\text{H}_2\text{O}$  molecules are reported in Table S3 of the Supporting Information. This table also provides these data for the six less-stable ZB complexes with  $\text{C}_s$  symmetry, one imaginary frequency, and out-of-plane  $\text{H}_2\text{O}$  molecules. Table 5 presents selected data for the more stable  $\text{C}_s$  complexes with in-plane  $\text{H}_2\text{O}$  molecules. The  $\text{P}\cdots\text{O}$

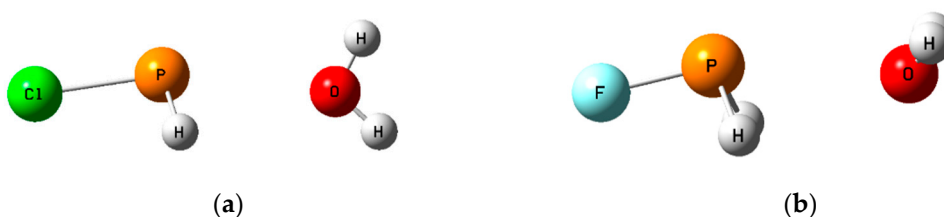


distances in these complexes range from 2.755 Å in  $\text{H}_2\text{FP}:\text{OH}_2$  to 3.036 Å in  $\text{H}_2(\text{CCH})\text{P}:\text{OH}_2$ . Their binding energies do not correlate well with the  $\text{P}\cdots\text{O}$  distances, as indicated by correlation coefficients of 0.7 for linear, quadratic, and exponential trendlines. The O-P-A angles, with A the atom of X directly bonded to P, are also reported in Table 5. These angles vary between 161 and 168°, indicating that the O-P-A arrangement approaches linearity. These values are consistent with the values of the P-P-A and N-P-A angles in the pnictogen-bonded complexes  $(\text{H}_2\text{XP})_2$  [44] and  $\text{H}_2\text{XP}:\text{NXH}_2$  [45].

**Table 4.** Binding energies of pnictogen-bonded complexes with  $\text{C}_1$  and  $\text{C}_s$  symmetries.

$\text{H}_2\text{XP}$ , X =	Equilibrium Symmetry	$\Delta E$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) for Equilibrium Structures	$\Delta E$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) for $\text{C}_s$ Structures with $\text{H}_2\text{O}$ in-Plane	$\Delta E$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) for $\text{C}_s$ Structures with $\text{H}_2\text{O}$ out-of-Plane
NC	$\text{C}_s$	−21.1	−21.1	−19.9 <sup>b</sup>
F	$\text{C}_1$	−19.5	−19.2 <sup>a</sup>	−18.5 <sup>b</sup>
Cl	$\text{C}_1$	−17.3	−17.2 <sup>a</sup>	−16.3 <sup>b</sup>
CN	$\text{C}_s$	−16.9	−16.9	−15.7 <sup>b</sup>
OH	$\text{C}_1$	−12.8	−12.4 <sup>a</sup>	−12.1 <sup>b</sup>
CCH	$\text{C}_s$	−11.3	−11.3	−10.1 <sup>b</sup>

<sup>a</sup> These  $\text{C}_s$  structures with water in-plane have one imaginary frequency; <sup>b</sup> These complexes with out-of-plane  $\text{H}_2\text{O}$  molecules have one imaginary frequency.



**Figure 5.** The pnictogen-bonded complexes  $\text{H}_2\text{ClP}:\text{OH}_2$  (a) with the  $\text{H}_2\text{O}$  molecule in the  $\text{C}_s$  symmetry plane; and  $\text{H}_2\text{FP}:\text{OH}_2$  (b) with  $\text{C}_s$  symmetry and an out-of-plane  $\text{H}_2\text{O}$  molecule.

Table 5 also presents the NBO  $\text{O}_{\text{lp}}\rightarrow\sigma^*\text{P-A}$  charge-transfer energies in these pnictogen-bonded complexes. Charge-transfer energies vary from 8  $\text{kJ}\cdot\text{mol}^{-1}$  in  $\text{H}_2(\text{CCH})\text{P}:\text{OH}_2$  to 20  $\text{kJ}\cdot\text{mol}^{-1}$  in  $\text{H}_2(\text{NC})\text{P}:\text{OH}_2$ . They exhibit an exponential dependence on the  $\text{P}\cdots\text{O}$  distance, with a correlation coefficient of 0.949.

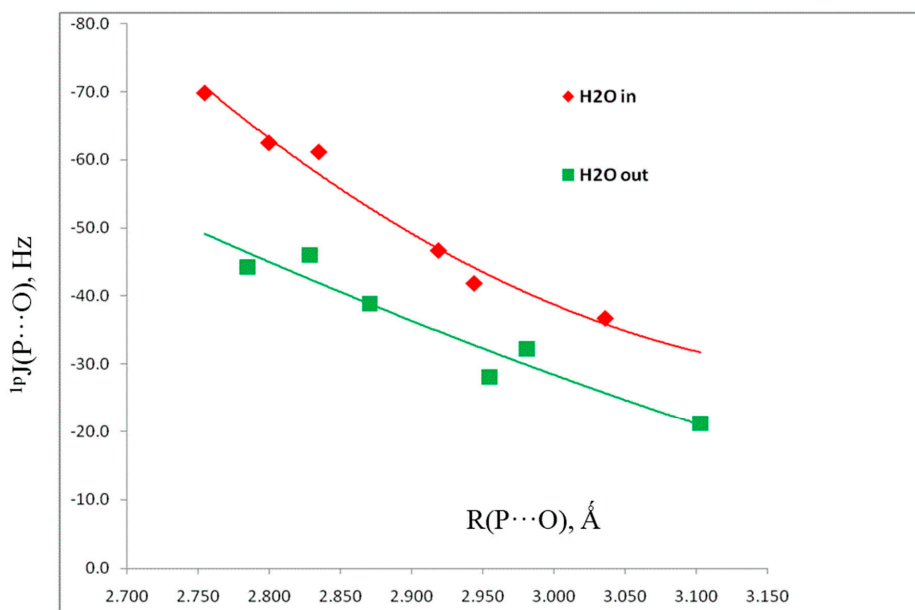
**Table 5.**  $\text{P}\cdots\text{O}$  distances, O-P-A angles, charge-transfer energies, and  $^1\text{PJ}(\text{P-O})$  coupling constants for pnictogen-bonded complexes  $\text{H}_2\text{XP}:\text{OH}_2$  with  $\text{C}_s$  symmetry and in-plane  $\text{H}_2\text{O}$  molecules.

$\text{H}_2\text{XP}$ , X =	Distance (R, Å)	Angles ( $\angle$ , °)	Charge-Transfer Energies ( $\text{kJ}\cdot\text{mol}^{-1}$ )	Coupling Constants (Hz)
	R( $\text{P}\cdots\text{O}$ )	$\angle\text{O-P-A}^a$	$\text{O}_{\text{lp}}\rightarrow\sigma^*\text{P-A}$	$^1\text{PJ}(\text{P-O})$
NC <sup>b</sup>	2.800	165	20.3	−62.5
F	2.755	167	19.5	−69.8
Cl	2.835	166	17.4	−61.2
CN <sup>b</sup>	2.944	161	12.3	−41.9
OH	2.919	166	11.6	−46.7
CCH	3.036	167	8.0	−36.7

<sup>a</sup> A is the atom of X directly bonded to P. <sup>b</sup> The atom written first is directly bonded to P.

Table 5 also reports the spin–spin coupling constants  $^1\text{PJ}(\text{P-O})$  across the pnictogen bonds. The components of these coupling constants are reported in Table S4 of the Supporting Information.  $^1\text{PJ}(\text{P-O})$  values are dominated by the Fermi-contact terms, and vary from −37 Hz in  $\text{H}_2(\text{CCH})\text{P}:\text{OH}_2$

to  $-70$  Hz in  $\text{H}_2\text{FP}:\text{OH}_2$ . Figure 6 illustrates the second-order dependence of  $^1\text{P}(\text{P}-\text{O})$  on the  $\text{P}\cdots\text{O}$  distance, with a correlation coefficient of 0.979.



**Figure 6.**  $^1\text{P}(\text{P}-\text{O})$  versus the  $\text{P}\cdots\text{O}$  distance for pnictogen-bonded complexes  $\text{H}_2\text{XP}:\text{OH}_2$  with  $\text{C}_s$  symmetry and in-plane and out-of-plane  $\text{H}_2\text{O}$  molecules.

A second reason for optimizing the set of complexes with  $\text{C}_s$  symmetry and out-of-plane  $\text{H}_2\text{O}$  molecules is to examine the coupling constants of these structures, the components of which are reported in Table S5. Since  $^1\text{P}(\text{P}-\text{O})$  values are also dominated by the Fermi-contact terms, it is expected that the s electron densities at O and at P interacting with O will be very different in the ground state and the excited states which couple to the ground state for these two orientations of  $\text{H}_2\text{O}$  molecules. It is apparent from Figure 6 that such is the case, since at the same  $\text{P}\cdots\text{O}$  distances, the points for structures with out-of-plane  $\text{H}_2\text{O}$  molecules lie below those for in-plane  $\text{H}_2\text{O}$  molecules.

Finally, a plot of  $^2\text{H}(\text{O}-\text{P})$  for hydrogen-bonded complexes and  $^1\text{P}(\text{P}-\text{O})$  for pnictogen-bonded complexes with  $\text{C}_s$  symmetry and in-plane  $\text{H}_2\text{O}$  molecules versus the  $\text{P}\cdots\text{O}$  distance is reported as Figure S1 of the Supporting Information. At the shorter  $\text{P}\cdots\text{O}$  distances, the absolute values of  $^2\text{H}(\text{O}-\text{P})$  are greater than the values of  $^1\text{P}(\text{P}-\text{O})$  at longer distances, but a single second-order trendline with a correlation coefficient of 0.981 describes the distance dependence of both coupling constants.

#### 4. Conclusions

Crystal structures have long been used as a tool for identifying and confirming the presence of weak intermolecular interactions, including hydrogen bonds and pnictogen bonds. A search of the CSD for complexes of water with phosphine and arsine identified two water–phosphine complexes stabilized by hydrogen bonds and one stabilized by a pnictogen bond, as well as three water–arsine complexes with hydrogen bonds and four with pnictogen bonds. The range of  $\text{P}\cdots\text{O}$  distances in the phosphine complexes is consistent with the results of *ab initio* MP2/aug'-cc-pVTZ calculations carried out on complexes  $\text{H}_2\text{XP}:\text{OH}_2$ , for  $\text{X} = \text{NC}, \text{F}, \text{Cl}, \text{CN}, \text{OH}, \text{CCH}, \text{H}$ , and  $\text{CH}_3$ . Only hydrogen-bonded complexes are found on the  $\text{H}_2(\text{CH}_3)\text{P}:\text{OH}_2$  and  $\text{H}_3\text{P}:\text{OH}_2$  potential surfaces, while only pnictogen-bonded complexes exist on the  $\text{H}_2(\text{NC})\text{P}:\text{OH}_2$ ,  $\text{H}_2\text{FP}:\text{OH}_2$ ,  $\text{H}_2(\text{CN})\text{P}:\text{OH}_2$ , and  $\text{H}_2(\text{OH})\text{P}:\text{OH}_2$  surfaces. Both hydrogen-bonded and pnictogen-bonded complexes are found on the  $\text{H}_2\text{CIP}:\text{OH}_2$  and  $\text{H}_2(\text{CCH})\text{P}:\text{OH}_2$  surfaces, with the pnictogen-bonded complexes more stable than the corresponding hydrogen-bonded complexes. It is apparent that the more electronegative



substituents prefer to form pnictogen-bonded complexes, while the more electropositive substituents form hydrogen-bonded complexes. The binding energies of pnictogen-bonded complexes range from  $-11$  to  $-21$   $\text{kJ} \cdot \text{mol}^{-1}$ , while the hydrogen-bonded complexes have binding energies from  $-9$  to  $-15$   $\text{kJ} \cdot \text{mol}^{-1}$ . The hydrogen-bonded complexes are stabilized by charge transfer from the lone pair on P to the antibonding  $\sigma^*$  H-O orbital, while pnictogen-bonded complexes are stabilized by charge transfer from the lone pair on O to the antibonding  $\sigma^*$  P-A orbital, with A the atom of X directly bonded to P.

Spin-spin coupling constants  $^2h(\text{O-P})$  and  $^1h(\text{H-P})$  correlate with the  $\text{O} \cdots \text{P}$  and  $\text{H} \cdots \text{P}$  distances, respectively, while  $^1J(\text{O-H})$  for the hydrogen-bonded O-H group increases in absolute value only slightly upon complex formation.  $^1J(\text{P-O})$  coupling constants were computed for two sets of pnictogen-bonded complexes, one with  $C_s$  symmetry and the  $\text{H}_2\text{O}$  molecule in the symmetry plane, and the other also with  $C_s$  symmetry but with an out-of-plane  $\text{H}_2\text{O}$  molecule.  $^1J(\text{P-O})$  for both sets are quadratically dependent on the  $\text{P} \cdots \text{O}$  distance. The different orientations of the  $\text{H}_2\text{O}$  molecule in these two sets alter the s electron densities at O and P, and lead to greater absolute values of  $^1J(\text{P-O})$  for complexes with in-plane  $\text{H}_2\text{O}$  molecules compared to those with out-of-plane  $\text{H}_2\text{O}$  molecules.

**Supplementary Materials:** Supplementary materials can be found at <http://www.mdpi.com/2073-4352/6/2/19/s1>.

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